

A note about the ground state of the H_3^+ hydrogen molecular ion

J. C. Lopez Vieyra,^{*} A.V. Turbiner,[†] and H. Medel[‡]

Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México,

Apartado Postal 70-543, 04510 México, D.F., Mexico

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Abstract

Three simple 7-, (7+3)-, 10-parametric trial functions for the H_3^+ molecular ion are presented. Each of them provides subsequently the most accurate approximation for the Born-Oppenheimer ground state energy among several-parametric trial functions. These trial functions are chosen following a criterion of physical adequacy and includes the electronic correlation in the exponential form $\sim \exp(\gamma r_{12})$, where γ is a variational parameter. The Born-Oppenheimer energy is found to be $E = -1.34034, -1.34073, -1.34159$ a.u., respectively, for optimal equilateral triangular configuration of protons with the equilibrium interproton distance $R = 1.65$ a.u. The variational energy agrees in three significant digits (s.d.) with most accurate results available at present as well as for major expectation values.

^{*}Electronic address: vieyra@nucleares.unam.mx

[†]Electronic address: turbiner@nucleares.unam.mx

[‡]Electronic address: medel@nucleares.unam.mx

I. INTRODUCTION

The two-electron hydrogenic molecular ion H_3^+ is one among the most abundant chemical compounds in the Universe. Its existence is of fundamental importance in chemistry and physics, in particular, because of its stability towards decay to $\text{H}_2 + p$, the H_3^+ ion is also a major proton donor in chemical reactions in interstellar space. The H_3^+ was discovered experimentally by J.J. Thomson in 1912 [1]. The system was very difficult for theoretical studies. Many theoretical methods were developed to study low-lying quantum states of this system. In particular, it became clear very quickly that interelectron correlation is of great importance and it should be included to the variational trial function explicitly which assure a faster convergence. This conclusion was similar to one drawn by James and Coolidge for the H_2 molecule. Usually, the interelectron correlation was written in the form r_{12}^n (Hylleraas [2] - James-Coolidge [3] form) or $\exp(-\alpha r_{12}^2)$ (Gaussian form, see e.g. Ref. [4]).

Recently, Korobov [5] showed in explicit way that for the case of Helium atom the use of exponential form $\exp(-\gamma r_{12})$ dramatically improves convergence and leads, in fact, to the most accurate results for the ground state energy for the Helium atom at present. Later on, it was shown that the similar use of exponential correlation $\exp(-\gamma r_{12})$ for the H_2 molecule allows to construct the most accurate trial function among few-parametric trial functions [6]. A hint why namely this r_{12} -dependence leads to the fast convergent results was given in [6]. In year 2006 an overwhelming discussion meeting took place in London, UK where different properties of the H_3^+ ion and, in particular, various theoretical approaches to study the H_3^+ ion were exposed (see [7]).

The goal of this Note is to propose a simple, compact, easy-to-handle trial function depending exponentially on r_{12} with few nonlinear parameters which leads to highly accurate Born-Oppenheimer ground state energy and major expectation values. We are not aware about previous studies of the H_3^+ ion with trial functions involving r_{12} in exponential form with a single exception [8] where the H_3^+ in linear configuration was explored.

In this paper atomic units ($\hbar = e = m_e = 1$) are used throughout, albeit energies are given sometimes in Rydbergs.

II. THE H_3^+ ION IN THE BORN-OPPENHEIMER APPROXIMATION

The Hamiltonian which describes the ion H_3^+ under the assumption that the protons are infinitely massive (the Born-Oppenheimer approximation of zero order) and located at the vertices of an equilateral triangle of side R (see Fig. 1 for the geometrical setting and notations), is written as follows:

$$\mathcal{H} = \sum_{j=1}^2 \hat{\mathbf{p}}_j^2 - \sum_{\substack{j=1,2 \\ \kappa=A,B,C}} \frac{2}{r_{j,\kappa}} + \frac{2}{r_{12}} + \frac{6}{R}, \quad (1)$$

where $\hat{\mathbf{p}}_j = -i\nabla_j$ is the 3-vector of the momentum of the j th electron, the index κ runs over protons A , B and C , $r_{j,\kappa}$ is the distance between the j th electron and the κ th proton, r_{12} is the interelectron distance, and R is the interproton distance.

It is a well established fact that the ground state of the H_3^+ molecular ion is $1^1A'_1$, an electronic spin-singlet state, with the three protons forming an equilateral triangle in the totally symmetric representation A'_1 of a D_{3h} point symmetry [9]. Thus, the ground state electronic wavefunction should be symmetric under permutations of the three indistinguishable protons. This ground state is the major focus of the present study.

It is worth mentioning that the best theoretical value at the moment for the Born-Oppenheimer ground state energy is $E = -1.34383562502$ a.u. [10] obtained with a basis of 1000 explicitly correlated spherical Gaussian functions with shifted centers. This value surpasses the previous record $E = -1.343835624$ a.u. by Cencek *et al.* which was obtained by using explicitly correlated Gaussian functions [11].

III. VARIATIONAL METHOD

The variational procedure is used as a method to explore the problem. The recipe of choosing the trial function is based on arguments of physical relevance, e.g. the trial function should support the symmetries of the system, has to reproduce the Coulomb singularities and the asymptotic behavior at large distances adequately (see, e.g. [12–14]). In practice, the use of such trial functions implies the convergence of a special form of the perturbation theory where the variational energy is the sum of the first two terms. Let us remind the essentials of this perturbation theory (for details, see [12–14]). Let us assume that our original Hamiltonian has a form $\mathcal{H} = -\Delta + V$. As a first step we choose a trial function

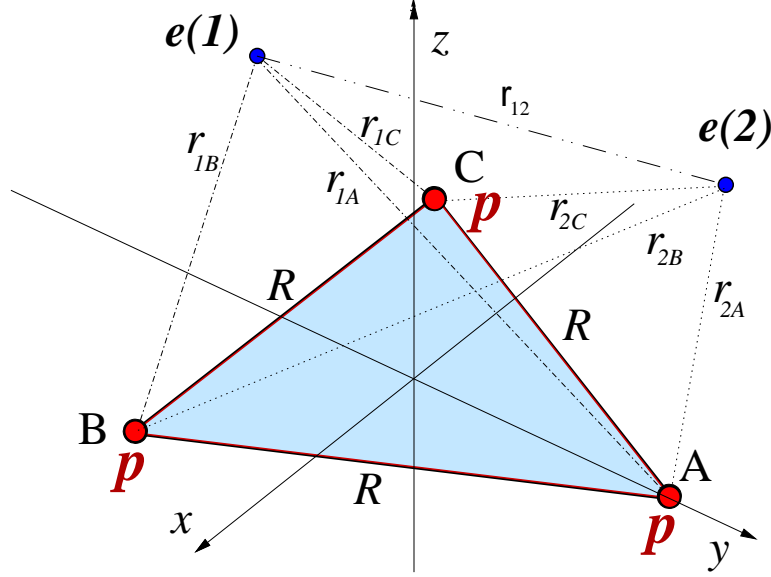


FIG. 1: Geometrical setting for the hydrogen molecular ion H_3^+ in equilateral triangular configuration. The three protons are located on the x - y plane forming an equilateral triangle with the origin of coordinates located at the geometrical center (circumcenter) of the triangle.

$\psi^{(trial)}$ (normalized to one) and find a potential for which such a trial function $\psi^{(trial)}$ is an exact eigenfunction, *i.e.* $V_{trial} = \Delta\psi^{(trial)}/\psi^{(trial)}$, with energy $E_{trial} = 0$. In a pure formal way we can construct a Hamiltonian $\mathcal{H}_{trial} = -\Delta + V_{trial}$ such that $\mathcal{H}_{trial}\psi^{(trial)} = 0$. It can be easily shown that the variational energy

$$E_{var} = \langle \psi^{(trial)} | \mathcal{H} | \psi^{(trial)} \rangle$$

is nothing but the first two terms in the perturbation theory where the unperturbed problem is given by \mathcal{H}_{trial} and the perturbation is the deviation of the original potential V from the trial potential V_{trial} , namely, $V_{perturbation} = V - V_{trial}$. Eventually, we arrive at the formula

$$E_{var} = E_{trial} + E_1(V_{perturbation}) , \quad (2)$$

here $E_1(V_{perturbation}) = \langle \psi^{(trial)} | V_{perturbation} | \psi^{(trial)} \rangle$ is the first energy correction in the perturbation theory, where the unperturbed potential is V_{trial} . It is worth noting that if the trial function is the Hartree-Fock function the resulting perturbation theory is nothing but the Moeller-Plesset perturbation theory (see, e.g. [16], Section 15.18)¹.

¹ It is worth noting that the question about a convergence of the Moeller Plesset perturbation theory is not settled yet [17]

One of the criteria of convergence of the perturbation theory in $V_{\text{perturbation}} = V - V_{\text{trial}}$ is a requirement that the ratio $|V_{\text{perturbation}}/V|$ should not grow when r tends to infinity in any direction. If this ratio is bounded by a constant it should be less than one. In fact, it is a condition that the perturbation potential is subordinate with respect to the unperturbed potential. The value of this constant controls the rate of convergence - a smaller value of this constant leads to faster convergence [13]. Hence, the above condition gives a importance to the large-range behavior of the trial functions. In the physics language the above requirement means that the phenomenon of the Dyson's instability should not occur (for a discussion see [12])².

IV. CORRELATED TRIAL FUNCTION

Among different forms to include explicit electronic correlation in the trial wave function for two-electron problems we mention three major approaches (see e.g. [18]): the linear in r_{12} , the gaussian $\exp(-\alpha r_{12}^2)$ and exponential $\exp(\gamma r_{12})$ terms. Among them, the factor $\exp(\gamma r_{12})$ only fulfills the adequacy requirements for a trial function described above. Thus, following the guidelines of Section III and the requirement of the convergence of the perturbation theory, we choose the trial function for the ground state in the following form:

$$\psi_0 = (1 + P_{12}) \sum_{\text{perm}\{A,B,C\}} e^{-\alpha_1 r_{1A} - \alpha_2 r_{1B} - \alpha_3 r_{1C} - \alpha_4 r_{2A} - \alpha_5 r_{2B} - \alpha_6 r_{2C} + \gamma r_{12}}, \quad (3)$$

where the sum runs over the permutations of the identical protons A, B, C (S_3 symmetry), and P_{12} is the operator which interchanges electrons ($1 \leftrightarrow 2$). The variational parameters consist of non-linear parameters α_{1-6} and γ which characterize the (anti)screening of the Coulomb charges. The interproton distance R , see Fig.1 is kept fixed. It is chosen to be equal $R = R_{eq} = 1.65 \text{a.u}$ [10-11]. The function (3) is a symmetrized product of $1s$ Slater type orbitals multiplied by the exponential correlation factor $e^{\gamma r_{12}}$.

Calculations of the variational energy were performed using the minimization package MINUIT from CERN-LIB. Six-dimensional integrals which appear in the functional of energy were calculated numerically using a "state-of-the-art" dynamical partitioning procedure: the

² It is worth noting that this procedure for a selection of the trial function was applied successfully to a study of one-two-electron molecular systems in a magnetic field leading to the highly accurate results. Many of these results are the most accurate at the moment (see [14] and [15]).

domain of integration was divided into 972 subdomains following the profile of the integrand, in particular, separating out the domains with sharp changes of the integrand. Then each subdomain was integrated separately in parallel manner with controlled accuracy (for details, see e.g. [14]). A realization of the routine required a lot of attention and care. During the minimization process the partitioning was permanently controlled and adjusted. Numerical integration of every subdomain was done with a relative accuracy of $\sim 10^{-3} - 10^{-7}$ depending on its complexity and relative contribution using an adaptive routine based on an algorithm by Genz and Malik [19] from R. Schürer's HIntLib C++ multidimensional integration library (<http://mint.sbg.ac.at/rudi/>). Parallelization was reached using the MPI standard library MPICH. Computations were performed on a Linux cluster with 48 Xeon processors of 2.67 GHz each, and 12Gb total RAM plus extra processor serving as the master node. Total minimization process took about 1000 hours of wall clock time when a single call took about three minutes. For optimal values of parameters it took about 20 minutes (wall clock time) to compute a variational energy with relative accuracy 10^{-7} .

V. RESULTS

In Table I we present the results for the ground state energy at interproton equilibrium distance of the H_3^+ molecular ion obtained by different researchers using different methods. In a clear way it is seen that the Born-Oppenheimer ground state energy obtained using the trial function (3) is the most accurate (the lowest) energy obtained with a few parametric functions. In particular, the trial function (3) gives a lower energy than the energies obtained with the explicitly correlated functions based on both Gaussians in r_{12} [20] and linear in r_{12} [21], when a relatively small number of terms with non-linear parameters is involved. The trial function (3) is more accurate than almost all(!) traditional CI calculations which were performed before 1971 (see [22]) even including one of the largest set of 100 configurations [24]. In those CI calculations no explicit correlation was included. The variational energy obtained with (3) is even of comparable accuracy to the large CI calculations [23, 24]³. Table II shows the optimal values of the variational parameters in (3).

The list of major expectation values obtained with the trial function (3) and its com-

³ for a list of 42 calculations of the ground state energy of H_3^+ in the period 1938-1992 see Ref.[22], for a list of selected *ab-initio* calculations till 1995, see [4]

parison with results of other calculations is given in Table III. A reasonable agreement for expectation values is observed. In particular, for the expectation values $\langle 1/r_{1A} \rangle$, $\langle x^2 \rangle$, $\langle z^2 \rangle$ and $\langle r^2 \rangle$ an agreement within $\sim 1\%$ with ours and all other calculations is observed, including ones obtained in the large CISD-R12 calculations [21]. Also, for the expectation value of $\langle 1/r_{12} \rangle$ we have an agreement in the first significant digit with other calculations being in closer agreement to the value obtained with the correlated Gaussian (unrestricted) wavefunction with 15 terms [20], while for the expectation values $\langle 1/r_{1A} \rangle$ and $\langle z^2 \rangle$ we observe an agreement with other calculations in 3 and 2 significant digits, respectively. These facts seem to indicate that the presented expectation values are very accurate, corroborating the quality of the trial function (3) giving 2-3 s.d. correctly. Perhaps, it is worth noting that in absence of any criteria about accuracy of the obtained expectation values we can only note about agreement of them obtained in different approaches.

VI. CONCLUSION

We presented a simple and compact 7-parametric variational trial function together with its possible natural generalization by addition of the Heitler-London (HL) type function. This function already provides surprisingly accurate Born-Oppenheimer energy for the ground state of such a complicated molecular system H_3^+ . It is chosen following a criterion of physical adequacy which suggests to take the electronic correlation in the form $\sim \exp(\gamma r_{12})$ where γ is a variational parameter. The minimum energy is found to be $E = -1.34034$ a.u. at an equilibrium interproton distance $R = 1.65$ a.u. This result for the energy is the most accurate among the values obtained with several parametric trial functions. In particular, it is more accurate than the energies obtained with the explicitly correlated approaches of Ref.[21] (linear in r_{12}) and that of Ref.[20] (Gaussian in r_{12}), when a relatively small number of terms and non-linear parameters are involved.

In a spirit of the approach presented in [6] (see also [5]) the trial function (3) can be modified by adding similar function, in particular, of the Heitler-London type:

$$\psi_{HL} = e^{-\tilde{\alpha}(r_{1A}-r_{1B}-r_{1C}-r_{2A}-r_{2B}-r_{2C})+\tilde{\gamma}r_{12}}, \quad (4)$$

where $\tilde{\alpha}, \tilde{\gamma}$ are parameters. The function (4) alone gives a dominant contribution to small

E (a.u.)	R (a.u.)	method	reference
-1.339 7	1.66	CI-GTO, > 120 configs	[25] (1970)
-1.306 29	1.65	GG, 3 terms, 5 non-linear params	[20] (1973)
-1.327 25	1.65	GG, 6 terms, 7 non-linear params	
-1.331 47	1.65	GG, 10 terms, 9 non-linear params	
-1.332 29	1.65	GG, 15 terms, 11 non-linear params	
-1.334 382	1.65	R12, 10s basis set	[21] (1993)
-1.334 632	1.65	R12, 30s basis set	
-1.340 34	1.65	7-Parametric Trial Function (3)	present
-1.340 5	1.6405	CI -GTO, 48 configs	[23] (1971)
-1.340 5	1.65	CI -STO, 100 configs	[24] (1971)
-1.340 73	1.65	(7+3)-Parametric Trial Function (5) ⁽ⁱ⁾	present
-1.341 59	1.65	10-Parametric Trial Function (5) ⁽ⁱⁱ⁾	present
-1.342 72	1.65041	CI-GTO, 108 terms	[27] (1985)
-1.342 784	1.6504	CI-GTO, 8s3p1d/[6s3p1d] basis set	[28] (1978)
-1.343 40	1.6504	CI-GTO, 10s4p2d basis set	[29] (1990)
-1.343 822	1.65	CI-GTO, 700 terms	[30] (1990)
-1.342 03	1.6504	CI with r12, 36 configs	[31] (1982)
-1.343 422	1.6504	CI with r12, 192 configs	[32] (1984)
-1.343 500	1.6504	CI with r12, 13s3p/[10s2p] basis set	[33] (1988)
-1.343 828	1.65	CI with r12, 13s5p3d basis set.	[34] (1990)
-1.343 835	1.65	R12, 30s20p12d9f basis set	[21] (1993)
-1.343 35	1.65	GG, 15 terms, 135 non-linear params	[20] (1973)
-1.343 835 624	1.65	GG, 600 terms	[11] (1995)
-1.343 835 625 02	1.65	ECSG, 1000 terms	[10] (2009)

TABLE I: A selection of the calculations for the Born-Oppenheimer ground state energy at equilibrium distance of H_3^+ . Record calculations of Ref. [10] (2009) and Ref.[11] (1995). CI denotes Configuration Interaction, STO - Slater Type Orbitals, GTO - Gaussian Type Orbitals, GG - correlated Gaussians (Gaussian Geminals), R12 - the CI calculation augmented by terms linear in r_{12} , ECSG - Explicitly Correlated Spherical Gaussian functions. ⁽ⁱ⁾ Trial Function (5) with the parameters of ψ_0 kept fixed and equal to ones found for (3), ⁽ⁱⁱ⁾ Trial Function (5) with all 10 parameters optimized.

E (Ry)	α_1	α_2	α_3	α_4	α_5	α_6	γ	A	$\tilde{\alpha}$	$\tilde{\gamma}$
-2.680 7	-0.00353	0.18548	1.4245	1.0471	0.15082	0.58912	0.21632	—	—	—
-2.681 4	"							-0.03000	0.47517	0.76398
-2.683 2	-0.00294	0.21022	1.3849	1.0199	0.17103	0.59084	0.26044	-0.51154	0.59589	0.86229

TABLE II: The ground state energy of H_3^+ at $R_{eq} = 1.65$ a.u. and the non-linear variational parameters in $[a.u.]^{-1}$ corresponding to the trial function (3), to the trial function (5) with parameters corresponding to ψ_0 fixed and to (5) with 10 optimized parameters.

interproton distances. Taking a linear superposition with (3)

$$\Psi = \psi_0 + A\psi_{HL}, \quad (5)$$

and making minimization with respect to parameters $A, \tilde{\alpha}$ and $\tilde{\gamma}$ only (see Table II) give an essential improvement in the energy (see Table I). In particular, this function, which contains $(7 + 3)$ variational parameters, allows us to get more accurate result for energy than one obtained in [24] within CI-STO with 100 configurations.

Releasing all 10 parameters in (5) (see Table II) we obtain further improved result (see Table I), although we are still unable to reproduce the fourth significant figure in the energy. However, the obtained energy is among the thirteen the most accurate variational results ever calculated so far. It is slightly worse than one obtained in [31] based on CI with r12 method with 36 configurations. The expectation values in Table III gradually change with move from one Ansatz to another seemingly demonstrating a convergence. It seems evident that taking a linear superposition of two (or more) functions (3) instead of (5) will improve essentially the variational energies. It will be done elsewhere. Undoubtedly, trial functions (3), (5) can be used to study potential energy surface. It is worth emphasizing that the main attraction of functions (3), (5) is their compactness.

The function (3) can be easily modified for a study of spin-triplet states and as well as the low-lying states with non-vanishing magnetic quantum number. A generalization to more-than-two electron molecular systems seems also straightforward.

Expectation Value	Trial Function (3) / (5) ⁽ⁱ⁾ / (5) ⁽ⁱⁱ⁾	Others
$\langle r_{12} \rangle$	2.0032	
	2.0013	
	1.9931	
$\langle 1/r_{12} \rangle$	0.6315	0.59415 ^a
	0.6304	0.62636 ^c
	0.6302	
$\langle 1/r_{1A} \rangle$	0.8548	0.85519 ^c
	0.8548	0.8553 ^e
	0.8549	
$\langle x^2 \rangle = \langle y^2 \rangle$	0.7711	0.75818 ^a
	0.7703	0.7595 ^b
	0.7666	0.75913 ^c
		0.75968 ^d
		0.7605 ^e
$\langle z^2 \rangle$	0.5399	0.54802 ^a
	0.5367	0.5451 ^b
	0.5337	0.54085 ^c
		0.54179 ^d
		0.5396 ^e
$\langle r^2 \rangle$	2.0822	2.06442 ^a
	2.0773	2.0640 ^b
	2.0669	2.05911 ^c
		2.06114 ^d

TABLE III: Expectation values (in a.u.) for the H_3^+ ion in its ground state obtained with the trial functions (3) and (5)^(i,ii). Corresponding results obtained with other methods are displayed for comparison. Coordinates x, y, z and r are measured from the center of the equilateral triangle formed by protons. ^a Ref.[23] CI-43; ^b CI wavefunction (I) in Ref.[24]; ^c Correlated Gaussian (unrestricted) wavefunction with 15 terms in Ref.[20]; ^d CI wavefunction in Ref.[26]; ^e CISD-R12 wavefunction with the 10s8p6d4f basis set in Ref.[21].

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